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THE GERMANIUM-OXYGEN SYSTEM

by

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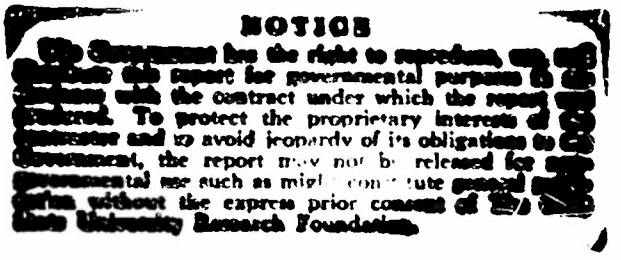
Technical Report



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FOREWORD

This work was carried out at The Ohio State University Cryogenic Laboratory under contract with U. S. Navy, Office of Naval Research Contract Number N6ori-17, Task Order IV, ONR Project Number NR 058 039, with The Ohio State University Research Foundation. This report covers information obtained during the study entitled: "High Temperature Thermodynamics of Inorganic Substances." It represents the 13th Technical Report of this series.

Director - - - Herrick L. Johnston

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ABSTRACT

High temperature x-ray diffraction patterns of germanium plus germanium oxide, GeO_2, between 750° and 1400° C, showed that germanium monoxide, GeO, is not a stable compound. At elevated temperatures germanium can dissolve up to 60 atom percent of oxygen. The oxygen causes first a slight expansion and then a contraction of the Ge lattice. At 850° and 930° C, the x-ray pattern of a germanium-oxygen compound, consisting of equimolecular quantities of germanium and oxygen, showed only the germanium pattern. At 1000° and higher (above the melting point of pure germanium, 965°C), the germanium pattern disappears, and liquid-like structure is visible, though the sample is still solid (melting point 1430°C). When the temperature is lowered again to 930°C, the germanium pattern reappears. The electrical resistivity of the Ge and GeO_2 mixture shows a sharp break at 970°C. In the germanium-oxygen compound we thus have a disordering of the germanium lattice above the melting point of pure germanium.

INTRODUCTION

The work of Buess and Wartenberg[1] and of Jolly and Latimer[2] showed that, when a mixture of germanium and germanium dioxide is heated in vacuum, germanium monoxide vaporizes. The solid is, as Jolly and Latimer point out, germanium plus germanium dioxide. A solid compound having the germanium-to-oxygen ratio of 1:1 can be prepared by precipitation from an aqueous solution of divalent germanium with alkali; this compound however is amorphous and thermodynamically unstable.

We proposed to investigate the possibility that GeO has a thermodynamically stable solid phase. For this purpose, we photographed x-ray diffraction patterns of a mixture of Ge and GeO_2 at various temperatures. If GeO is stable at any temperature, then the reaction $Ge(s) + GeO_2(s) \rightleftharpoons 2GeO(s)$ proceeds to the right. The x-ray diffraction patterns of germanium and germanium dioxide should disappear, and a new pattern, that of GeO, should appear. This, however, was not the case. We found that oxygen is very soluble in germanium, and therefore determined the lattice parameter of germanium as a function of the oxygen content.

Finally, we measured the electrical resistivity as a function of temperature for pure germanium dioxide and for the germanium-germanium dioxide mixture.

EXPERIMENTAL PROCEDURE

The method of obtaining the high-temperature x-ray diffraction patterns has been described elsewhere.[3] We want to emphasize that the x-ray samples are compressed rods, 0.03 in. in diameter, 0.25 in. long, which are not contained in a holder but stand by themselves.

For the determination of the lattice constants, the mixture of germanium and germanium dioxide was heated in a helium atmosphere for two hours at 750°C, then rapidly quenched. An x-ray diffraction pattern was photographed in a Norelco 119 mm diameter camera, using Ni-filtered copper K_α radiation. The lattice constants of germanium were determined from the [4, 4, 4] and [7, 1, 1] lines by the method suggested by Cohen.[4]

For the electrical resistivity measurements, the finely pulverized materials were pressed into a quartz tube, 1.25 in. long, 0.60 in. ID. Two platinum wires serving as leads were pushed in to the ends of the material. A Pt-PtRh thermocouple was fastened onto the outside of the quartz tube. This assembly was placed into a larger quartz tube, through which helium or air could be passed. The heating was done in a muffle furnace, and the heating and cooling speeds were 5° per minute between 700° and 1000°C. The resistance was measured with a Leeds and Northrup resistance box.

The germanium and germanium oxide were obtained from The Fairmount Chemical Company.

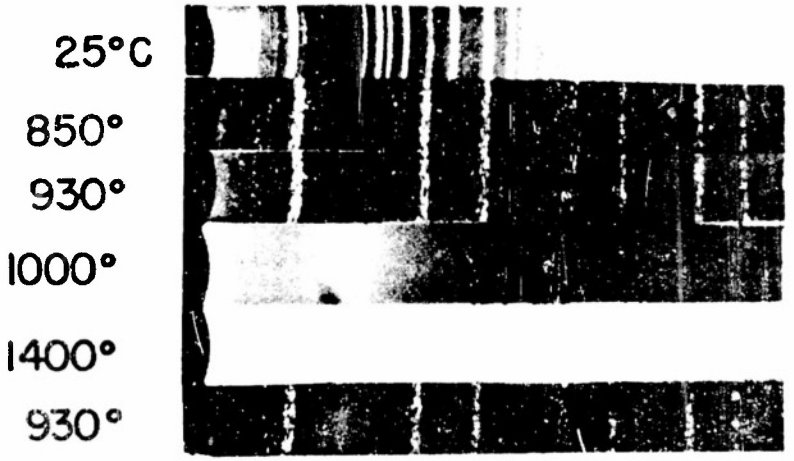
EXPERIMENTAL RESULTS

The GeO_2 was in the hexagonal form and heating it to 900° C for 24 hours, in the presence of a small amount of germanium, did not transform it into the tetragonal form. X-ray diffraction patterns obtained at 870°C, 975°C, and 1090°C showed only the GeO_2 diffraction lines.

Fig. 1 shows the x-ray diffraction patterns of a 1:1 mixture of Ge and GeO_2, obtained at various temperatures. At 25° C the Ge and GeO_2 lines are both present. At 850° and 930°C only the Ge diffraction pattern is visible. In the patterns taken at 1000° and 1400° C (above the melting point of pure germanium), a liquid-like structure is visible, although the sample is solid. (A liquid sample would melt and crumble down, because the sample is self-supported.) When the temperature is lowered again to 930° C, the germanium diffraction pattern reappears. The melting point taken in the x-ray camera was found to be 1430°C. The rate of solution of GeO_2 in Ge is strongly temperature dependent. At 750°C, 1-1/2 hours are needed to obtain complete solution (disappearance of GeO_2 diffraction lines); at 850°C the solution is completed in 30 minutes.

Table I contains the measured lattice constants of germanium for various oxygen contents, and the data are plotted in Fig. 2. Germanium can dissolve up to 60 atom percent oxygen interstitially.

Figure 3 shows the results of the resistivity measurements; log R is plotted against 1/T. The data on Ge + GeO_2 were taken



X-RAY DIFFRACTION PATTERNS OF Ge + GeO_2, SHOWING THE DISSOLUTION OF O IN Ge AND THE DISORDERING OF THE Ge LATTICE ABOVE THE MELTING POINT OF PURE Ge.(965°C)

FIG. 1

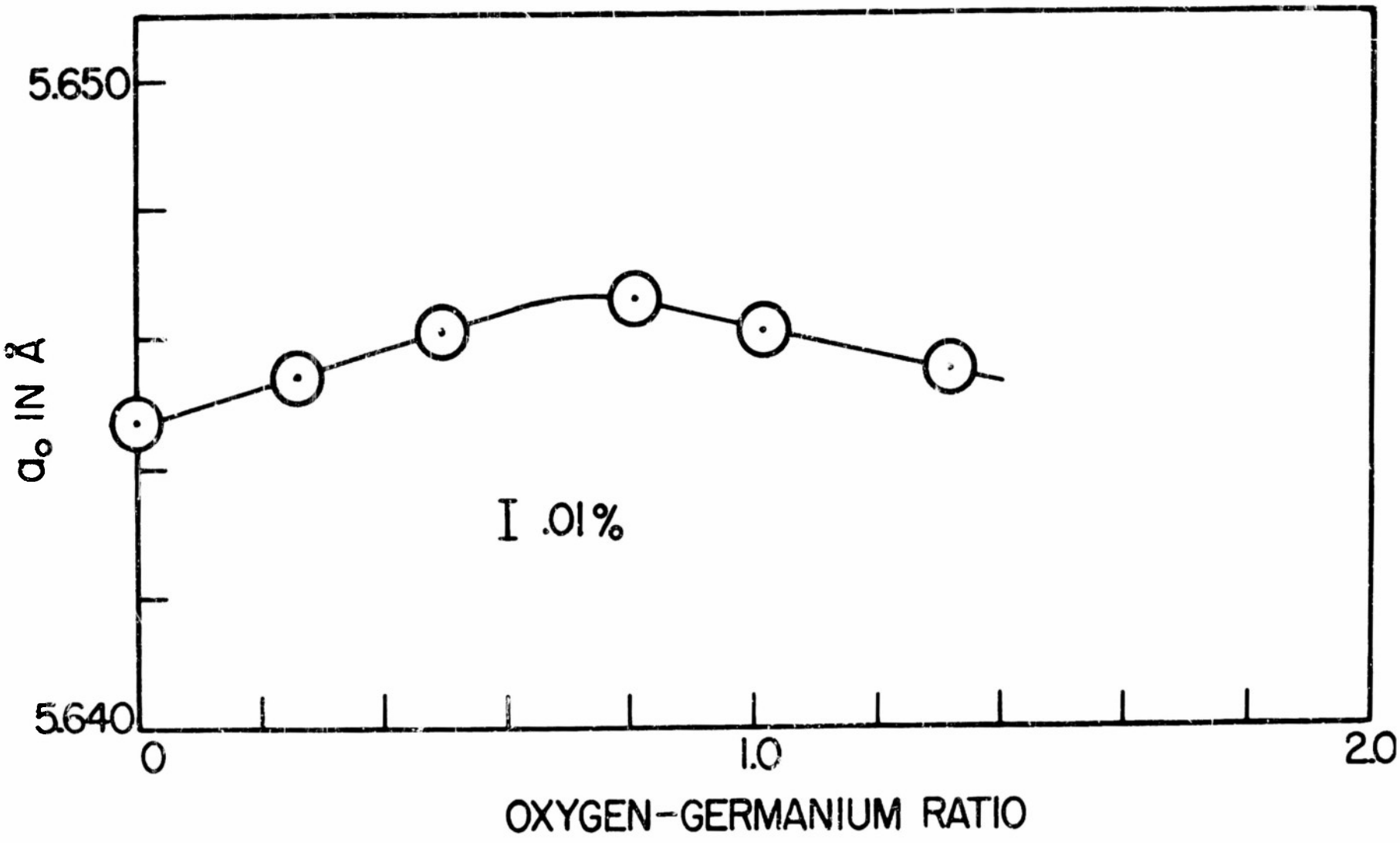


FIG. 2

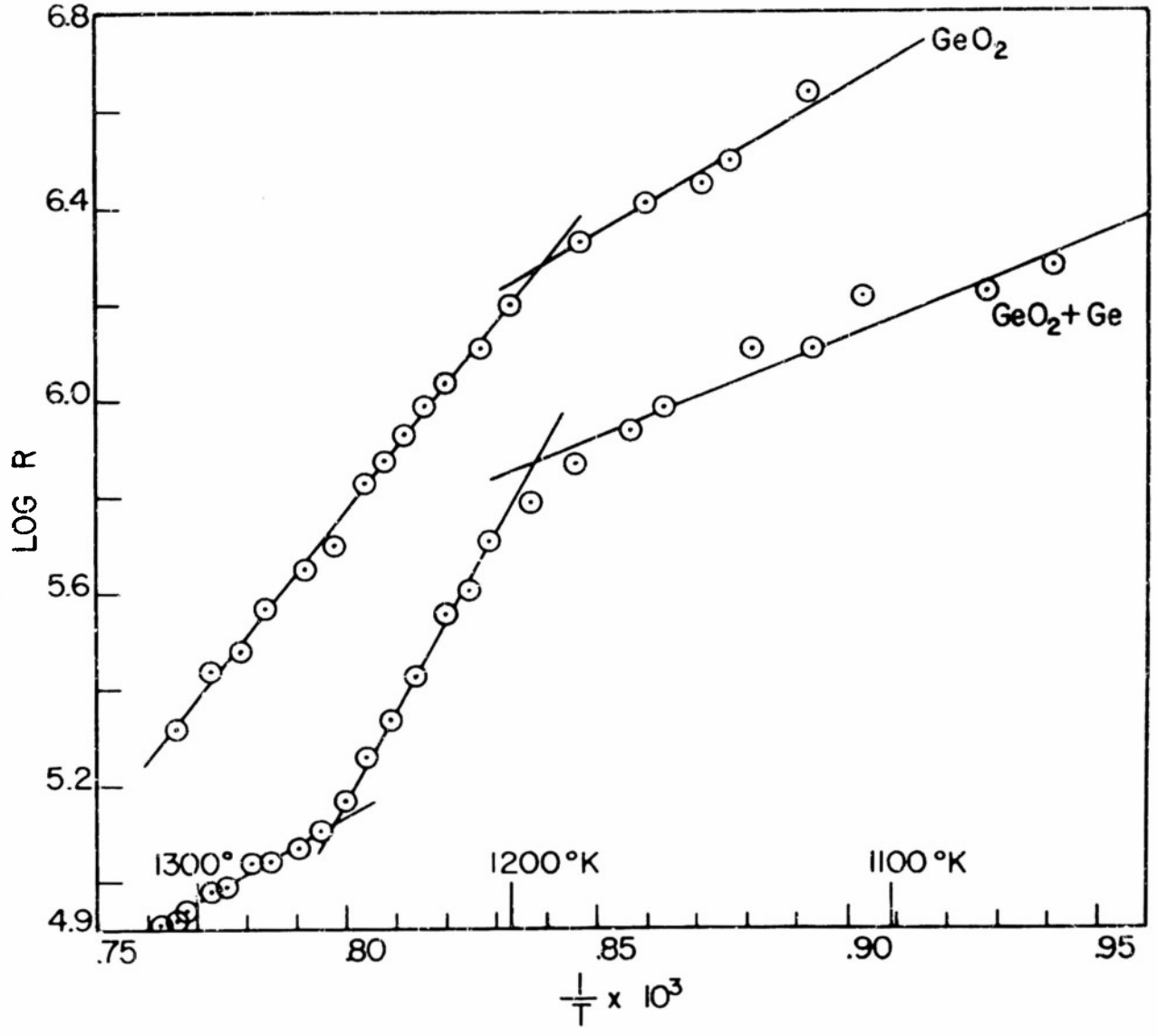

6.8
6.4
6.0
5.6
5.2
4.9
LOG R
GeO2
GeO2+ Ge
1300°
1200°K
1100°K
.75
.80
.85
.90
.95
1/T x 10^3

FIG. 3

in a helium atmosphere;the data on Ge + GeO_2 were taken in a helium atmosphere; the data on GeO_2 were taken in air to avoid loss of oxygen from the GeO_2. One set of measurements (not shown) was taken on GeO_2 in a helium atmosphere. The curve had two breaks, similar to that of Ge + GeO_2. The low-temperature break, present in both GeO_2 and Ge + GeO_2, occurs at 920°C; the high-temperature break is present only in Ge + GeO_2 and occurs at 970° C.

TABLE I

LATTICE CONSTANTS OF GERMANIUM
AS A FUNCTION OF THE OXYGEN CONTENTS

Atomic Ratio Ge:O	a_{CO} in A units
1:0.000	5.6447 ± .0004
1:0.2575	5.6454 ± .0004
1:0.495	5.6461 ± .0004
1:0.81	5.6466 ± .0004
1:1.02	5.6461 ± .0004
1:1.32	5.6455 ± .0004

DISCUSSION OF RESULTS

The high-temperature x-ray diffraction patterns show that, in the temperature range 850° - 1400°C, solid germanium monoxide is not a stable compound. From the work of Jolly and Latimer it follows that below 600° solid GeO is not stable either. The solid solution of oxygen in germanium melts at 1430° C. We can conclude from this that solid GeO has no stability range. From the disappearance of the GeO_2 x-ray diffraction pattern (when Ge + GeO_2 are heated together) it follows that above 750° C Ge can dissolve up to 60 atom percent of oxygen. The oxygen first causes a slight expansion of the germanium lattice, but when its concentration in-

creases, a contraction occurs, due to strong attracting forces between the germanium and oxygen.

The disappearance of the germanium lattice in x-ray diffraction patterns of a compound with a composition Ge:O = 1:1, taken above 965°C (the melting point of pure Ge), indicates that a transition or disordering of the Ge lattice takes place. It may be a random change of place between the germanium and oxygen atoms in the lattice. This change of place, if rapid and frequent enough, would destroy any x-ray diffraction patterns. It is very probable that the frequency of exchange of places increases strongly at the melting point of pure germanium. The break in the resistivity curve of GeO_2 + Ge, occuring at 970°C (melting point of germanium) substantiates the above-mentioned reasoning. The break in the resistivity, occuring at 920°C and present in pure GeO_2, is probably due to the oxygen and therefore would not show up in the x-ray diffraction pattern.

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